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"Microemulsion Formulation of Agricultural Adjuvants," by Curtis M. Elsik et al., 6th Int'l Symposium on Adjuvants for Agrochemicals, ISAA 2001, pages 403-408, (August 13-17, 2001).

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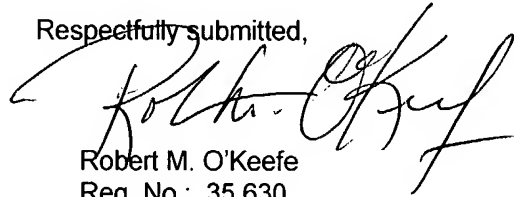
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MICROEMULSION FORMULATION OF AGRICULTURAL ADJUVANTS

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SUMMARY

Agricultural adjuvants are becoming an integral part of pesticide applications. In many cases, more than one type of adjuvant may be required to produce the desired efficacy. A microemulsion formulation should be considered as an option when water-soluble and oil-soluble components can be combined into a single convenience package. The advantages of this strategy are given, as well as ways to evaluate the robustness of the system. An example is provided to show that a successful microemulsion formulation is possible even when the water phase includes high electrolyte concentrations.

Key words: microemulsion, formulation, evaluation, surfactant, adjuvant.

INTRODUCTION

Agricultural adjuvants can be grouped into two main classes. There are oil-soluble, or lipophilic types such as crop oils, crop oil concentrates, petroleum oils, and other oils. There are also water-soluble, or hydrophilic types including nonionic surfactants, spreaders or wetting agents, and surfactants used for other purposes. In many applications it may be desired to combine two or more individual adjuvants.

In fact, commercial products already exist that combine fertiliser with crop oil and petroleum oils, and ammonium sulphate (AMS) combined with other adjuvants (1). In these examples, with the inclusion of fertiliser or ammonium sulphate, the aqueous phase has a high concentration of electrolyte.

As in the case with pesticide actives themselves, there are several formulation types that could be used to combine oil-soluble and water-soluble adjuvant components. These include Water in Oil Emulsions (EO), Oil in Water Emulsions (EW), and Suspoemulsions (SE). These formulations provide a kinetically stable product at best. Another formulation type to consider that provides a thermodynamically stable product is the microemulsion. The benefits of microemulsions as delivery systems for agricultural pesticides have been well articulated in the past (2).

DISCUSSION

Oil, surfactant, and electrolyte containing adjuvants may be combined into one package as a microemulsion formulation to provide a product that is at a thermodynamic equilibrium. A microemulsion eliminates the physical separation problems associated with macroscopic emulsions caused by creaming, sedimentation, flocculation, Ostwald ripening, and coalescence. There are several other attributes that can make the difficulties of formulating a microemulsion well worth the effort.

A microemulsion has a clear appearance. It is optically isotropic and can be transparent to translucent depending on particle size. The dispersed phase generally consists of droplets ranging in size from 10 to 200 nm.

Microemulsions form spontaneously within the appropriate temperature range. No special production equipment is required, and energy input into the process is relatively low. These factors combine to yield a relatively low processing cost to produce a commercial microemulsion formulation. Process scale-up is relatively easy with microemulsions versus the other colloidal formulation types.

One of the key advantages of a microemulsion is its thermodynamic stability. Over a given temperature range there will be no separation into bulk phases. Kinetic effects can be ignored as long as chemical stability of one of the components is not an issue. Even after a temperature transient, such as a freeze/thaw cycle, the microemulsion usually reforms spontaneously with little or no agitation. These factors increase the shelf life of a microemulsion formulation and make it a better candidate for bulk storage applications. They can be stored indefinitely and are stable to shear at constant composition and temperature.

Microemulsions have lower viscosities than their macroemulsion counterparts. In fact, viscosities are typically less than 500 cP. This means that the product will pour more easily out of the container. More importantly, it will empty the jug more completely and this will help minimise waste.

Multiple actives can be formulated into a microemulsion system. Oil soluble components can be included in the oil phase. Water soluble components can be included in the water phase. Targeted adjuvant surfactants can be included in the mix as long as the microemulsifier system is adjusted to allow for them.

It is usually a good plan to have the microemulsion concentrate dilute to a microemulsion at spray tank concentrations. The efficacy of a microemulsion can be at a maximum due to several factors. The bloom is usually excellent, and if the product dilutes to a microemulsion then the physical stability of the spray tank composition will be at an optimum.

The ultrafine particle size distribution of a microemulsion can provide enhanced efficacy (2). This feature can reduce the application rate of active ingredients. It could also reduce adjuvant requirement as well if the adjuvant dilutes to a microemulsion in the spray tank. The efficacy of each formulation should be evaluated on a case-by-case basis. The only way to achieve a more uniform application distribution than a microemulsion would be to have each component present as a true solution.

Typical Microemulsion Formulation

The generic composition of a representative oil in water microemulsion adjuvant is given in Table 1. When the oil system is the disperse phase, its volume loading is typically limited to less than 40 v/v%. The oil and aqueous phases can contain more than one component each. The emulsifier system can be a complex mixture of anionic and nonionic surfactants. The inclusion of a cosurfactant, or cosolvent, is usually

essential to produce ultralow interfacial tensions between the oil and aqueous phases. The highly curved interface of the dispersed phase requires that the interfacial tension be minimal for the system to exist in a thermodynamically stable state. The successful formulation of a microemulsion can become more challenging when the aqueous phase contains a very high loading of electrolyte.

TABLE 1. Typical Oil-in-Water Microemulsion Adjuvant Formulation

Component (w/w%)		Composition
Oil	5-30	Oil soluble adjuvants: crop oil, petroleum oil.
Aqueous	50-90	Water, water soluble adjuvants, fertiliser, AMS
Emulsifier	5-20	Blend of anionic and nonionic surfactants
Cosurfactant	0-5	(Cosolvent) short chain alcohol. amine

Microemulsion Formulation Development

There are several strategies used to develop microemulsion formulations. The simplest method is titration with cosurfactant. Start with the desired composition of oil, aqueous phase, and emulsifier system. This composition will be two phases prior to cosurfactant addition. Add the cosurfactant with mild agitation. If the overall composition is favourable, a microemulsion will form spontaneously when enough cosurfactant has been added.

The emulsifier system can be chosen for an oil-in-water (o/w) microemulsion using the HLB concept if the required HLB of the oil phase is known. The HLB of an o/w emulsifier is usually 8-18, which means a hydrophilic system will be required. Formulating a water-in-oil (w/o) microemulsion will require a lipophilic surfactant composition with a combined HLB around 3-8. A robust microemulsion usually requires a combination of anionic and nonionic surfactants in the emulsifier system. This approach blends the temperature performance of the anionic surfactant with the electrolyte tolerance of the nonionic surfactant.

The cosurfactant, or cosolvent choice is usually a short-chain alcohol for o/w microemulsions and a medium-chain alcohol for w/o microemulsions. Microemulsions can be formulated without cosurfactant if needed. In this case, the emulsifier system should depend heavily on nonionic surfactants.

Another method some researchers have used to prepare microemulsions is an adaptation of the phase inversion temperature (PIT) method used to make fine emulsions (3). Care must be taken when using this technique, as it is possible to produce a kinetically stable fine emulsion with a translucent appearance that is not a true thermodynamically stable microemulsion.

Microemulsion Evaluation/Optimisation

Once a successful microemulsion phase has been formulated, several parameters can be studied to optimise the formulation. It is important to look at dilution of the concentrate at the appropriate application rates, taking water hardness and temperature into consideration. Minimising the sedimentation rate and maximising bloom will lead the formulator to the most robust formulation possible.

The optimal application condition occurs when the microemulsion concentrate dilutes to a microemulsion. In this situation, sedimentation or any other type of separation is eliminated and the adjuvant system will be applied in a most efficacious manner. The bloom in this case will also be excellent.

The haze or clarity of the formulation can be measured. The haze will go down and the clarity up as microemulsion particle size is reduced. This procedure can be used to fine tune a formulation composition to achieve the smallest dispersed particle size possible.

A major concern when developing a microemulsion formulation is the upper and lower phase transition temperatures. The microemulsion is only thermodynamically stable over a finite temperature range. Above and below certain temperatures, the system will cloud as a second phase precipitates. This second phase will eventually separate on standing, and could lead to non-uniform applications in the field.

It is possible to move this temperature range up or down by changing the emulsifier system. The challenge is to move the upper phase change temperature higher while at the same time moving the lower phase change temperature colder. The optimised microemulsion formulation will have the broadest equilibrium temperature range possible.

Temperature transients are to be expected during long term storage. One of the key advantages of a microemulsion is that once the temperature is brought back to within its equilibrium range, the single phase microemulsion will reform. Each formulation should be evaluated to see if this happens spontaneously. If not, only minor agitation should be required to reform the microemulsion.

Other criteria to study are the freeze/thaw behaviour, the chemical stability of any active ingredients, and the physical stability or shelf life of the system. The formulation should be monitored for any precipitation or phase separation, which could be an indication of chemical instability in the system. Care must be taken when performing accelerated storage stability studies where temperature induced phase separations may cause misleading results.

MICROEMULSION ADJUVANT FORMULATION

The following system listed in Table 2 was chosen to demonstrate the cosurfactant titration technique of developing a microemulsion adjuvant formulation. The mixture combines a crop oil, emulsifier, compatibility agent and ammonium sulphate into one convenient package that exists as a single phase.

TABLE 2. Oil-in-Water Microemulsion Adjuvant Formulation Example

Component	(w/w%)	Composition
Oil	20	Sun 7N, Sun Oil Co.
Water	43	Water
AMS	20	Ammonium Sulphate
Emulsifier	1 5	Surfactant system: 9% anionic + 6% nonionic
Cosurfactant	2	Cosolvent

Figure 1 shows the classical Winsor types I, II and III microemulsion phase behaviour of this system as cosurfactant is slowly added (4). The initial separation into a Winsor type II system is shown in sample A before adding any cosurfactant. This two phase regime is a w/o microemulsion in equilibrium with an excess water phase. Sample B shows the formation of a Winsor type III system when 20% of the total cosurfactant required in the final composition has been added. This region is a middle phase microemulsion in equilibrium with an upper excess oil phase and a lower excess water phase. The middle phase microemulsion is a bicontinuous phase.

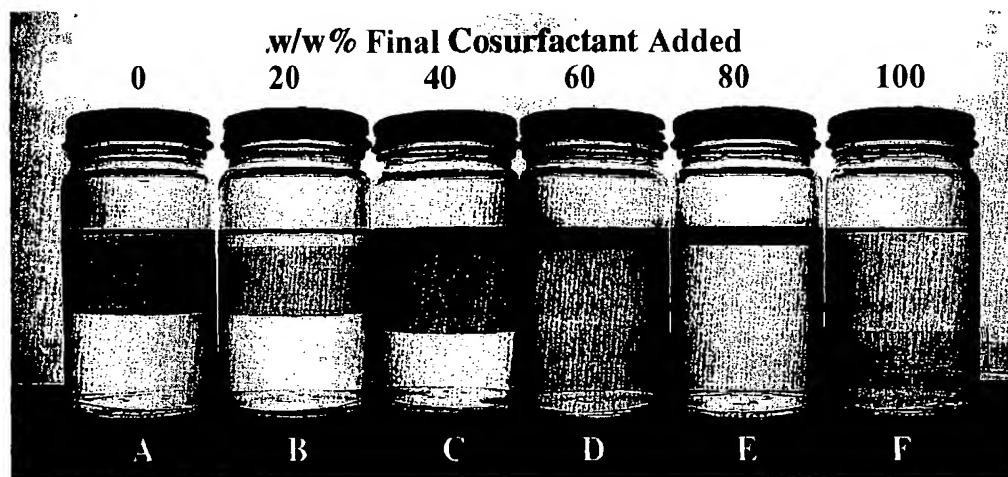


FIGURE 1. Equilibrium Phase Behaviour with Increasing Cosurfactant

Sample C is another example of Winsor type III phase behaviour. The upper excess oil phase clouds at 40% addition of the total required cosurfactant. Sample D illustrates a major phase transition to Winsor type I behaviour at 60% of the final cosurfactant. An o/w microemulsion is now in equilibrium with an excess oil phase, Sample E shows this excess phase disappearing as cosurfactant reaches 80% of the final composition.

The final Sample F shows the system becomes a single phase o/w microemulsion when all of the required cosurfactant has been added. A ruler was placed behind Sample F in Figure 1 to demonstrate the clarity of the microemulsion phase. It is easy to read the ruler through this transparent formulation.

There are other processing parameters the formulator can measure to monitor the microemulsion formation. Conductivity measurements can be used to show whether the system is water continuous or oil continuous. The pH can also be monitored when the surfactant system HLB is a function of pH. Figure 2 shows data for this example microemulsion system plotted as a function of the amount of final cosurfactant added. The data points in Figure 2 correspond to the samples shown in Figure 1.

Low initial conductivity during agitation means that this system starts out as an oil continuous mixture. Both conductivity and pH increase with the addition of cosurfactant as the surfactant system becomes more hydrophilic and the middle phase structure is formed. The surfactant eventually prefers the aqueous phase, and the continuous phase inverts from oil to water to form an o/w microemulsion.

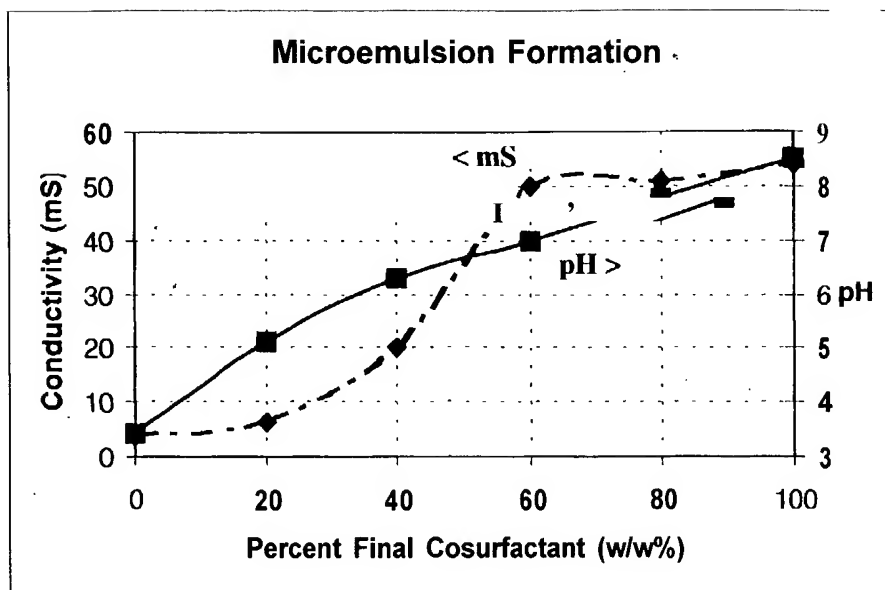


FIGURE 2. Conductivity and pH as a Function of Cosurfactant

CONCLUSIONS

Adjuvant systems that combine oil and aqueous components into a single convenience package can be successfully formulated as single phase microemulsions. This is true even when the aqueous phase contains a significant amount of electrolyte such as fertiliser or ammonium sulphate.

Microemulsion formulations can provide physical and efficacy advantages that make the difficult formulation development well worth the effort. They are at thermodynamic equilibrium and deliver extended physical stability, especially when compared to macroscopic emulsions.

One of the primary concerns that has impeded the adoption of microemulsions as commercial formulations in the past has been the cost associated with the relatively high concentration of surfactants. These costs can actually be offset by the reduction of other raw material costs in pesticide formulations. Many adjuvant applications, however, already contain high levels of surfactant. The challenge then becomes making the surfactants being used as wetting agent/spreader, oil emulsifier or compatibility agent also play a role as microemulsifier in the microemulsion adjuvant combination formulation.

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